Multinuclear complexes of metal phthalocyanines and related macroheterocycles with transition metals and clusters

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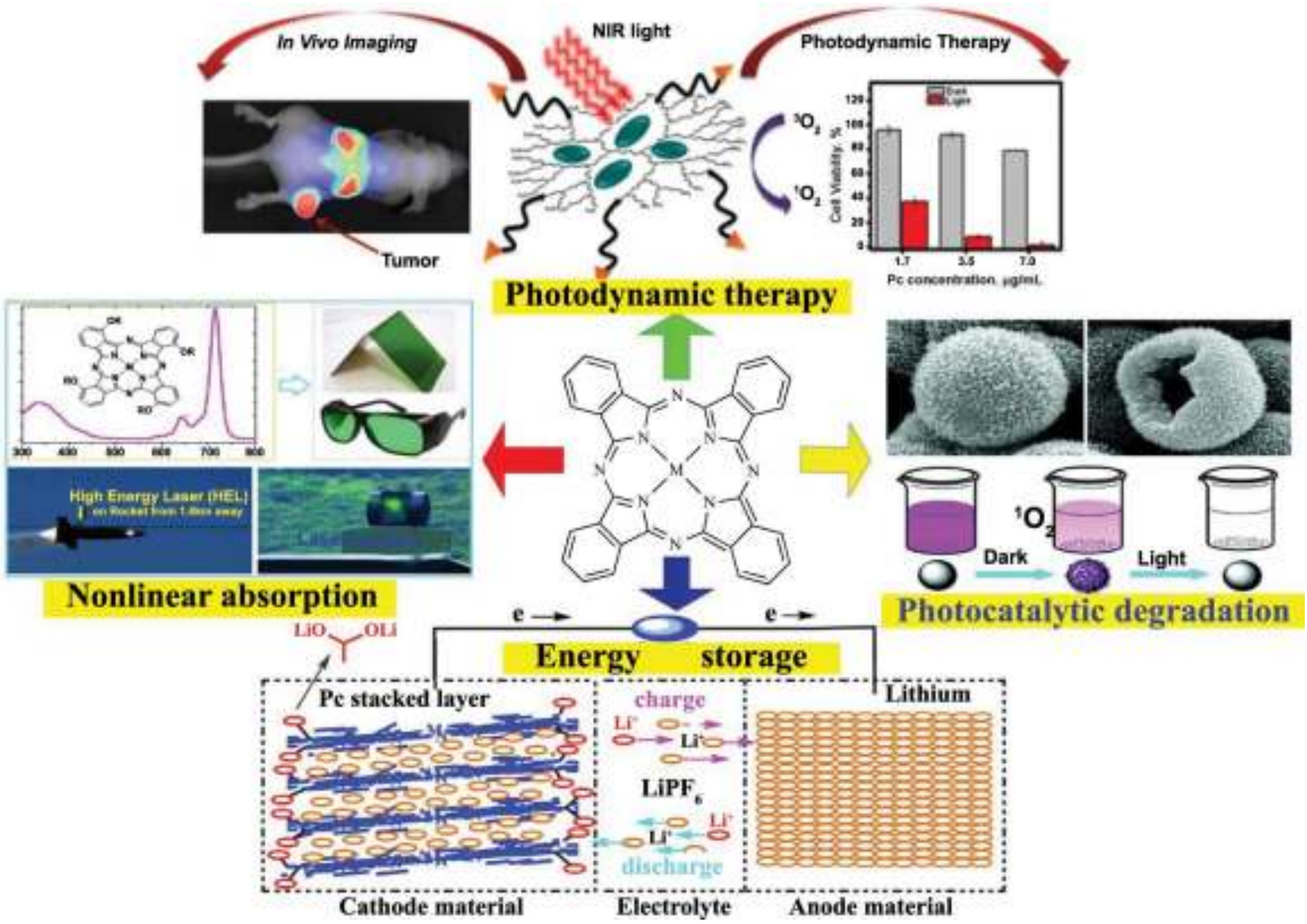
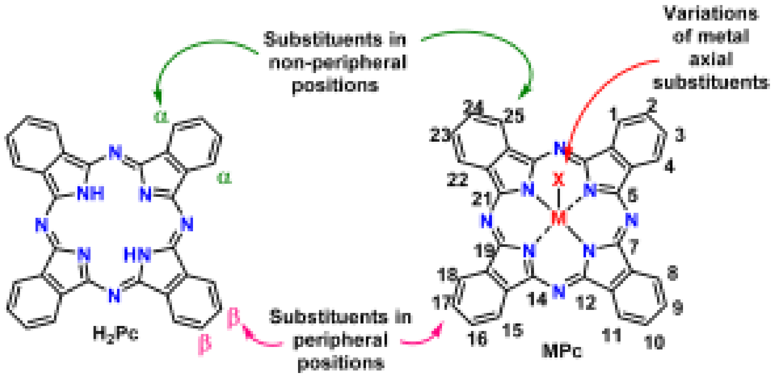
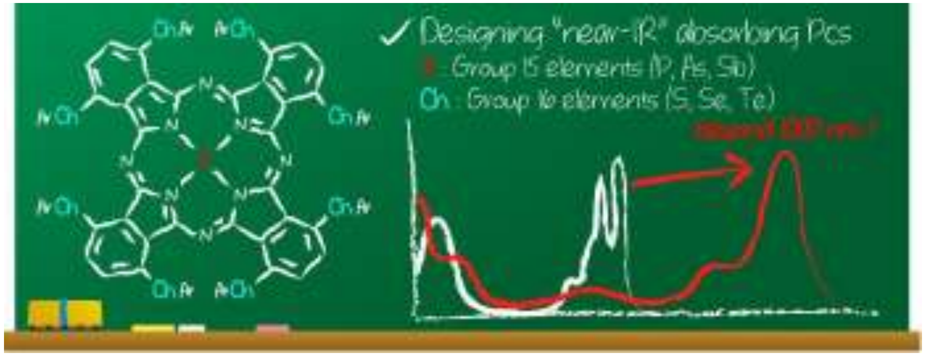
Phthalocyanines

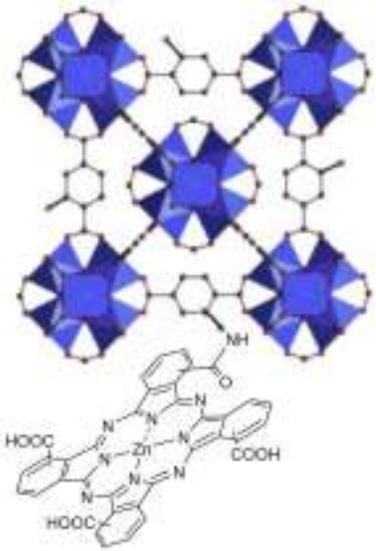


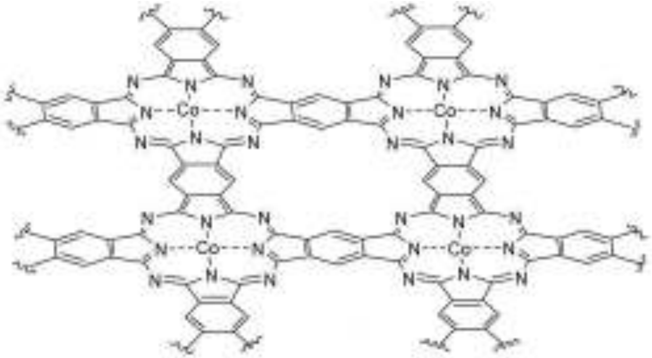
Current Organic Chemistry, 22, 485 – 504 (2018)

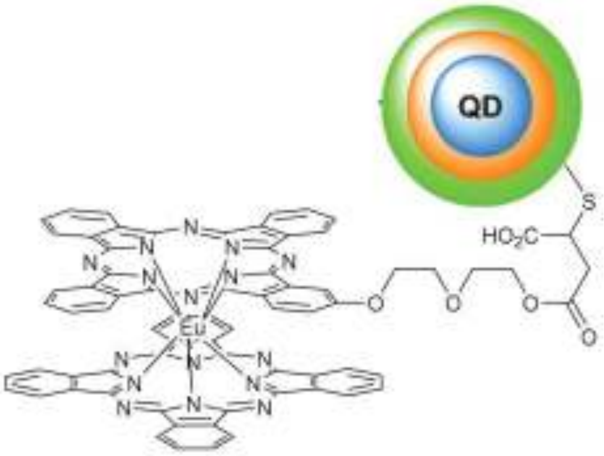
Phthalocyanines





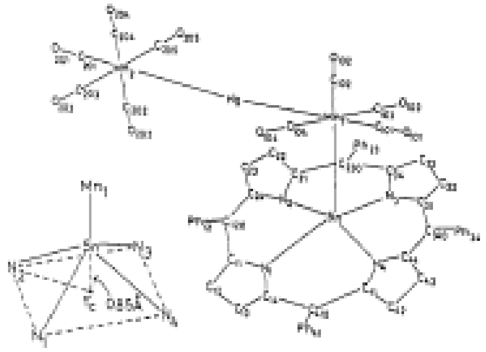




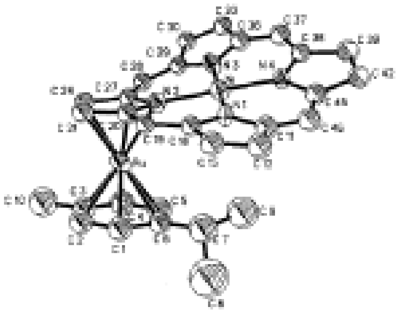


Molecules, 26, 2823 (2021)
J. Am. Chem. Soc., 136, 2, 765–776 (2014)

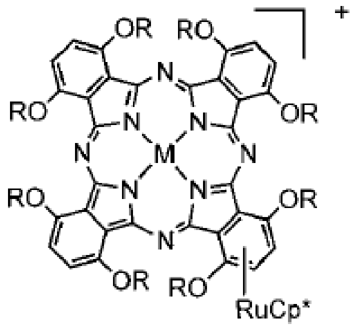
Coordination complexes



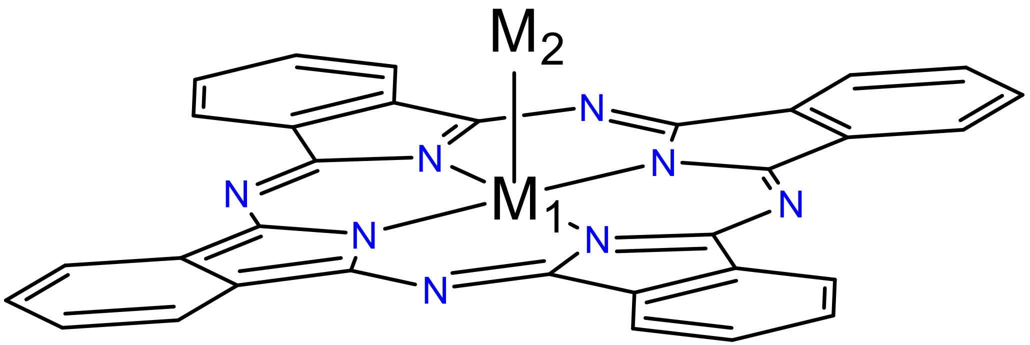
(TPP)Sn-Mn(CO)$_4$-Hg-Mn(CO)$_5$
Inorg. Chem., 24, 1070-1076 (1985)



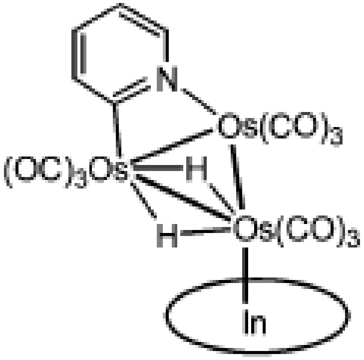
[(η ^{6}-cymene)Ru{η ^{5}-Ni(OEP)}](BF$_4$)$_2$
Angew. Chem. Inr. Ed., 35, 1833 (1996)



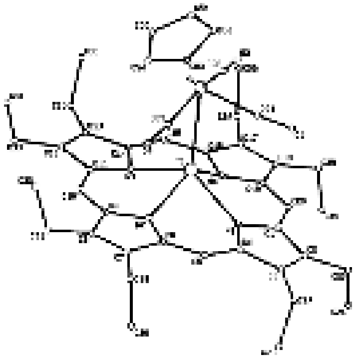
[(η ^{6}-cymene)Ru{η ^{5}-Ni(OEP)}](BF$_4$)$_2$
Organometallics, 19, 4767-4774 (2000)



Crystalline coordination σ-complexes of phthalocyanines haven’t been described yet

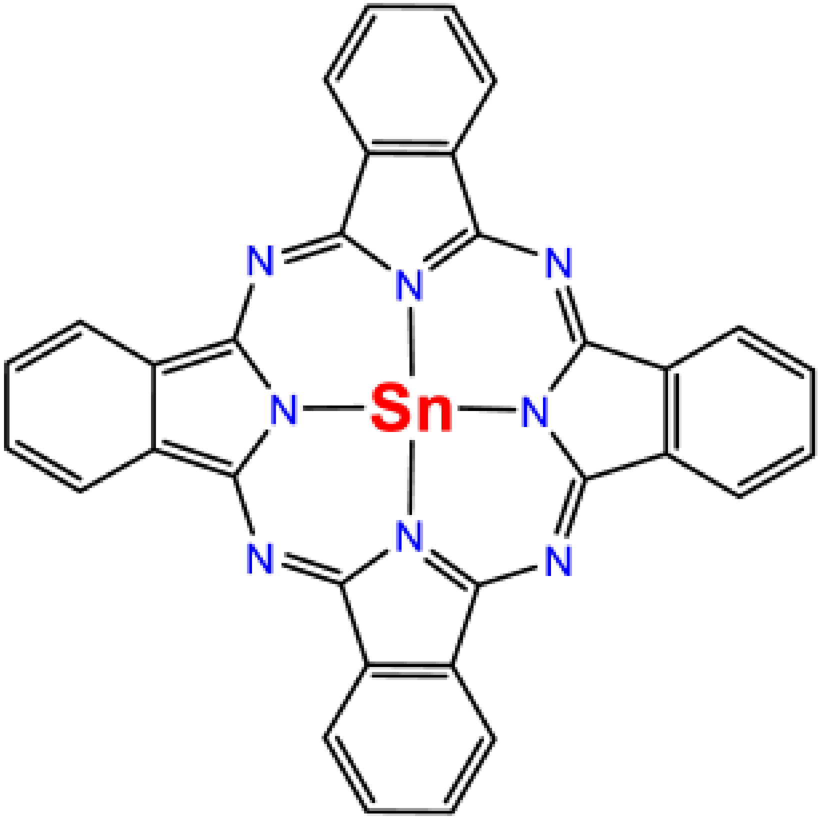


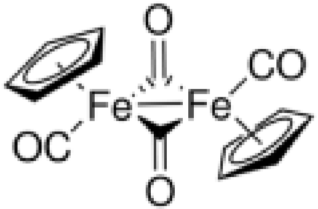
[(TPP)InOs$_3$(μ-H)$_2$(CO)$_9$(μ- η^2-C$_5$H$_4$N)]
Chem. Commun., 15, 1882–1883 (2003)

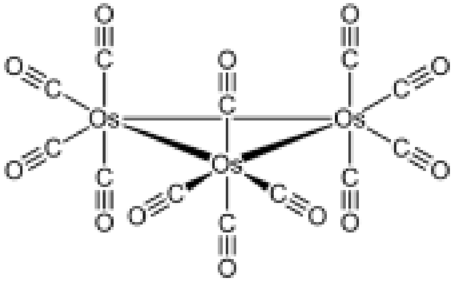


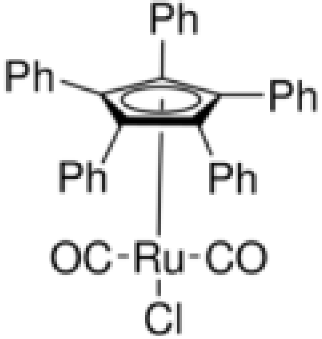
[(OEP)TlMo(CO)$_3$Cp]
Acta Cryst., C45, 1224—1226 (1989)

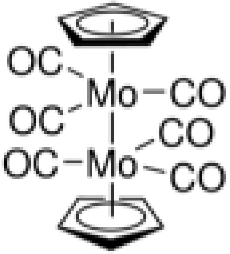
Coordination complexes of pthalocyanines

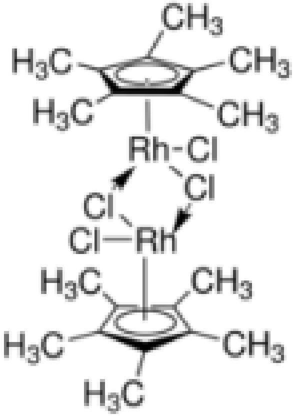




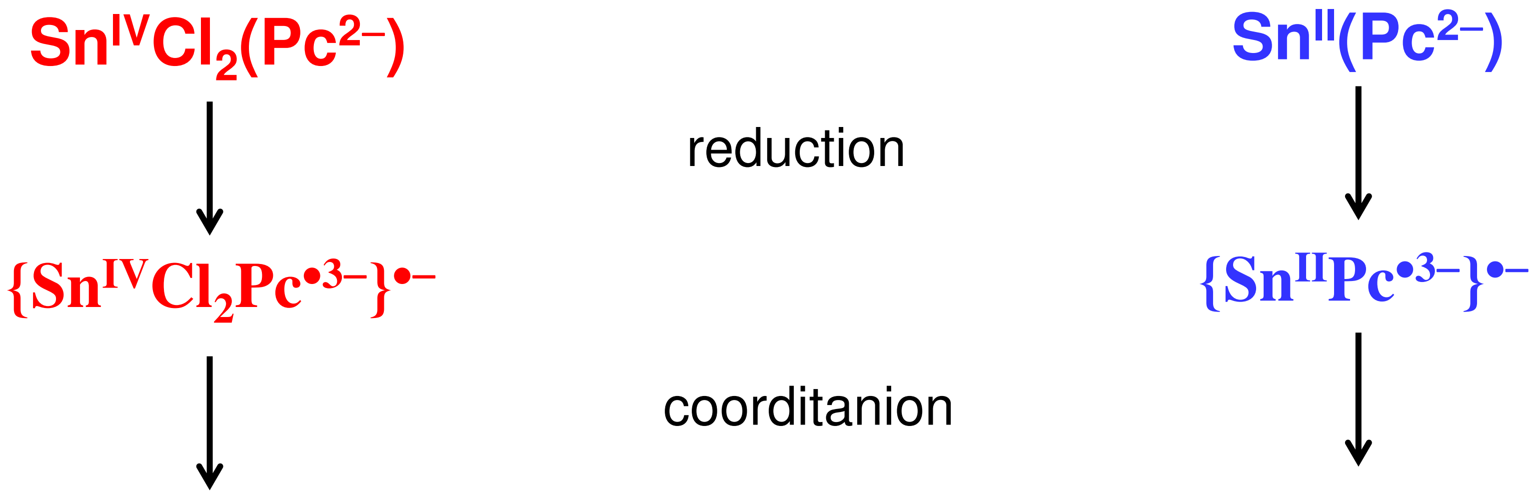








Synthesis



$Sn^{IV}Cl_2(Pc^{2-})$

$Sn^{II}(Pc^{2-})$

reduction

$\{Sn^{IV}Cl_2Pc^{\bullet 3-}\}^{\bullet -}$

$\{Sn^{II}Pc^{\bullet 3-}\}^{\bullet -}$

coorditanion

COMPLEXES WITH NEUTRAL MACROCYCLE

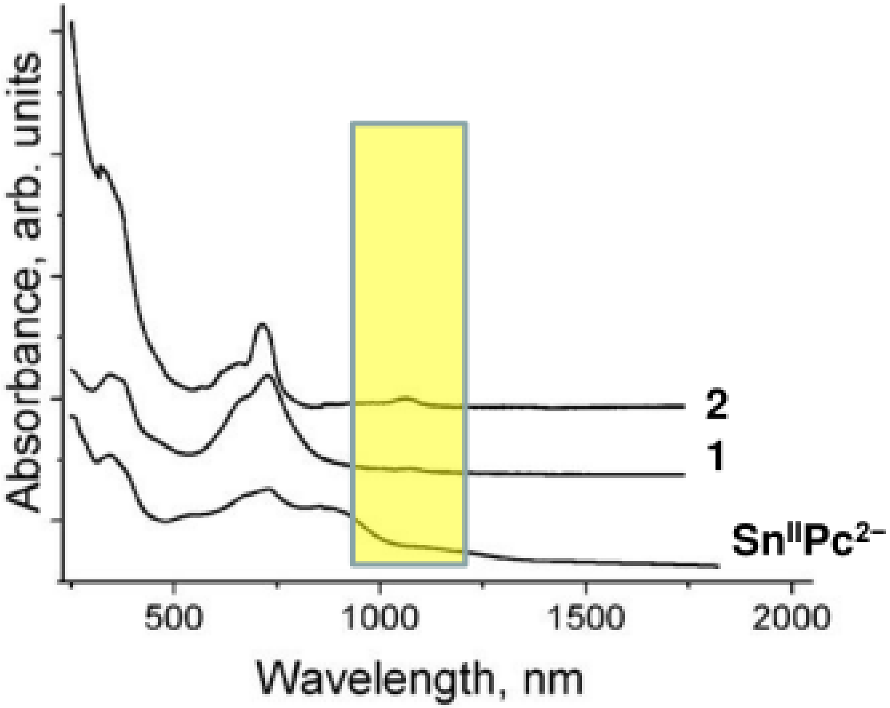
1	$Cp^{*}\mathbf{Mo}(Br)_{0.83}(CO)_{1.78}\mathbf{[Sn^{II}Pc^{2-}]}$
2	$Cp\mathbf{Fe}(CO)_2[\mathbf{Sn^{II}Pc^{2-}}]$

COMPLEXES WITH REDUCED MACROCYCLE

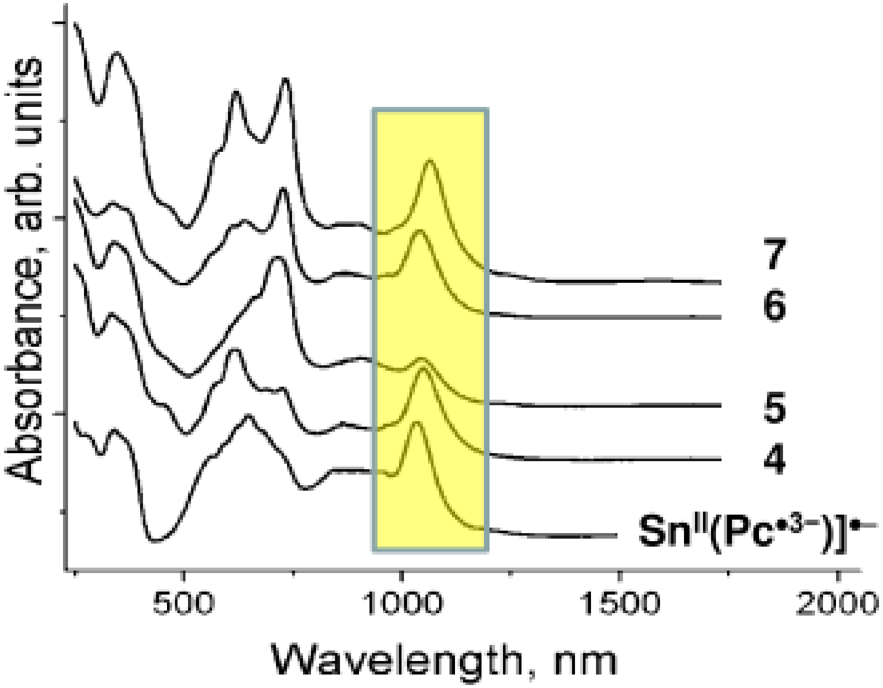
3	$\{cryptand(Na^+)\}\{Cp\mathbf{Fe}(CO)_2\mathbf{[Sn^{II}P^{4-}]}\}^-$
4	$\{cryptand(Na^+)\}\{\mathbf{Fe}(CO)_4\mathbf{[Sn^{II}(Pc^{\bullet 3-})]^{\bullet -}}\}$
5	$\{cryptand(Na^+)\}\{Cp\mathbf{Mo}(CO)_2\mathbf{[(Sn^{II}Pc)_2]^{\bullet -}}\}$
6	$\{cryptand(Na^+)\}\{Cp^{*}\mathbf{Rh}Cl_2\mathbf{[Sn^{II}(Pc^{\bullet 3-})]^{\bullet -}}\}$
7	$[Ph_5Cp\mathbf{Ru}(CO)_2\mathbf{Sn^{II}(Pc^{\bullet 3-})}]^0$
8	$\{Cryptand(Na^+)\}\{\mathbf{Ru}_3(CO)_{11}\cdot\mathbf{Sn^{II}(Pc^{\bullet 3-})}\}^-$
9	$\{Cryptand(M^+)\}_2\{\mathbf{Ru}_3(CO)_{10}\cdot\mathbf{[Sn^{II}(Pc^{\bullet 3-})]_2}\}^{2-}$

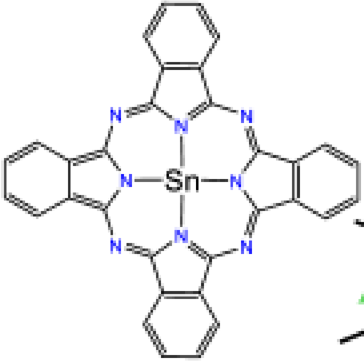
Properties of complexes

NEUTRAL MACROCYCLE

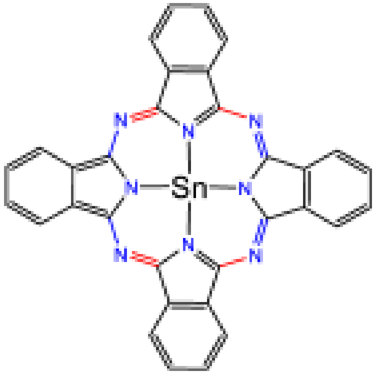


REDUCED MACROCYCLE





~~ALTERNATION~~



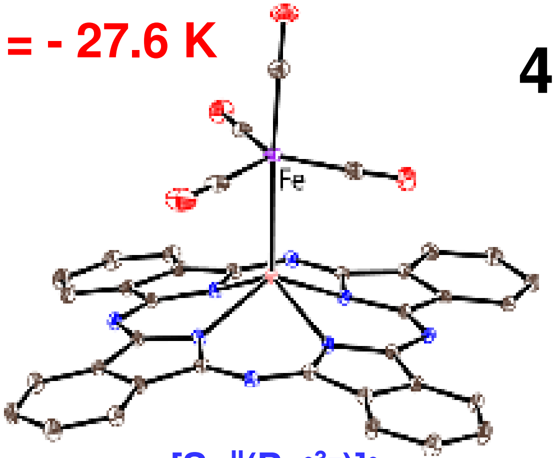
Short

Long

ALTERNATION

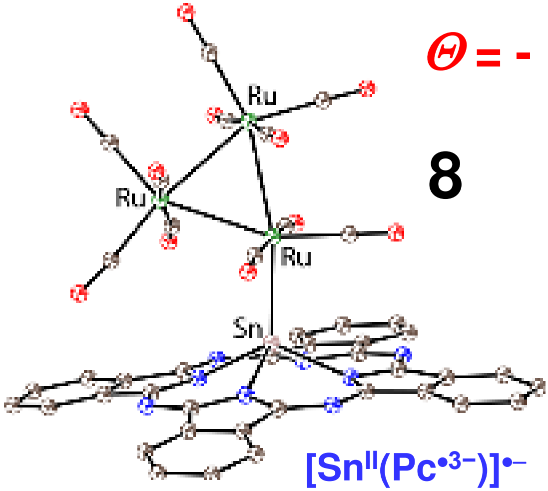
Magnetic properties

Θ = - 27.6 K



4

$[\mathrm{Sn^{II}(Pc^{\bullet 3-})}]^{\bullet -}$

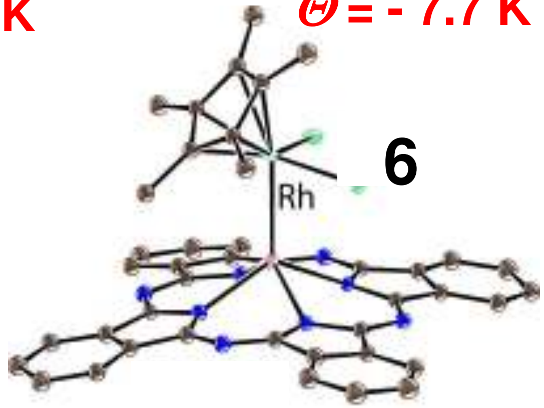


Θ = - 18 K

8

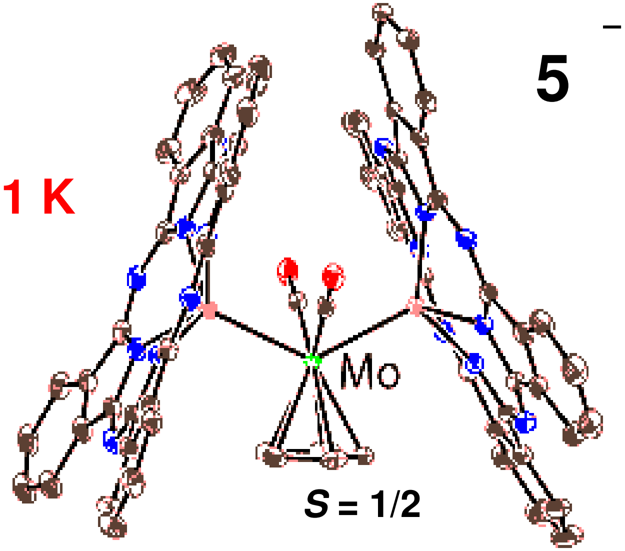
$[\mathrm{Sn^{II}(Pc^{\bullet 3-})}]^{\bullet -}$

Θ = - 7.7 K



6

$[\mathrm{Sn^{II}(Pc^{\bullet 3-})}]^{\bullet -}$



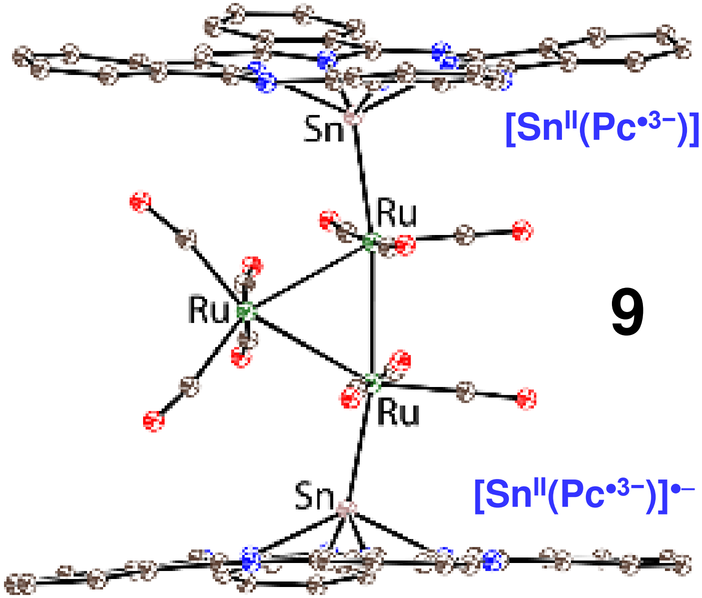
5 $^{-}$

Θ = - 28.1 K

S = 1/2

$[\mathrm{Sn^{II}(Pc^{\bullet 3-})}]^{\bullet -}$

$[\mathrm{Sn^{II}(Pc^{2-})}]$



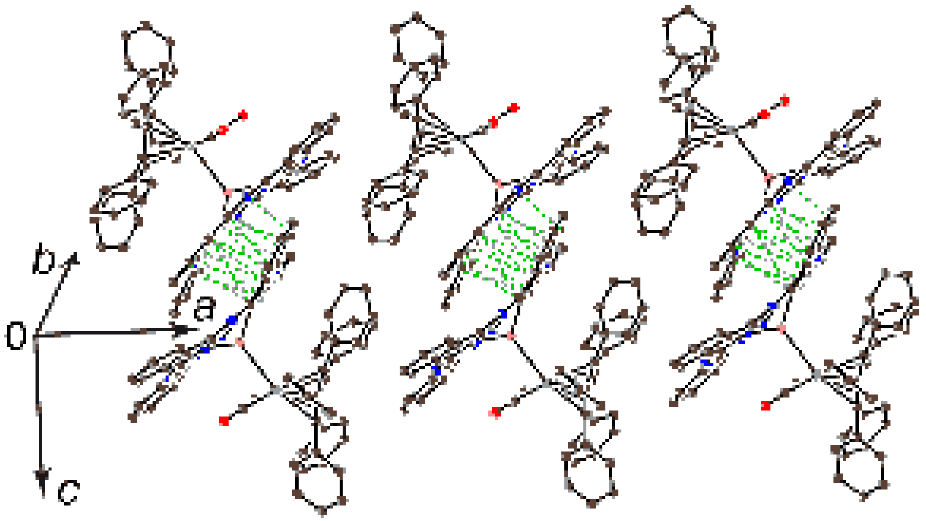
$[\mathrm{Sn^{II}(Pc^{\bullet 3-})}]^{\bullet -}$

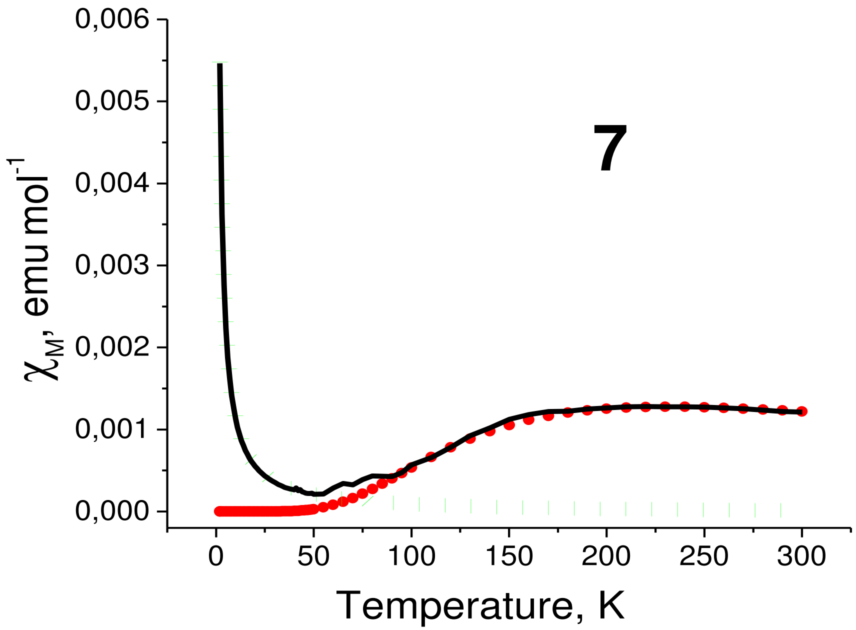
9

$[\mathrm{Sn^{II}(Pc^{\bullet 3-})}]^{\bullet -}$

Complex [$Ph_5Cp\mathbf{Ru^{II}}(CO)_2\mathbf{Sn^{II}(Pc^{\bullet 3-})}]^0$ (**7**)

$$\mathbf{[Sn^{II}(Pc^{\bullet 3-})]^{\bullet -} + Ph_5CpRu(CO)_2Cl} \xrightarrow{\mathbf{-\ Cl^-}} Ph_5Cp\mathbf{Ru^{II}}(CO)_2\mathbf{[Sn^{II}(Pc^{\bullet 3-})]}\ (\mathbf{7})$$





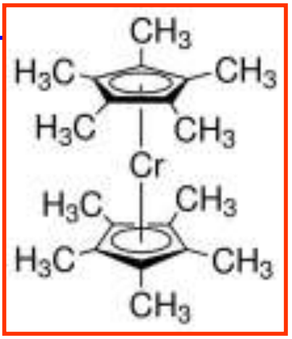
Strong interaction between radical anions $Pc^{\bullet 3-}$ in dimers

J/k_B = -183 K

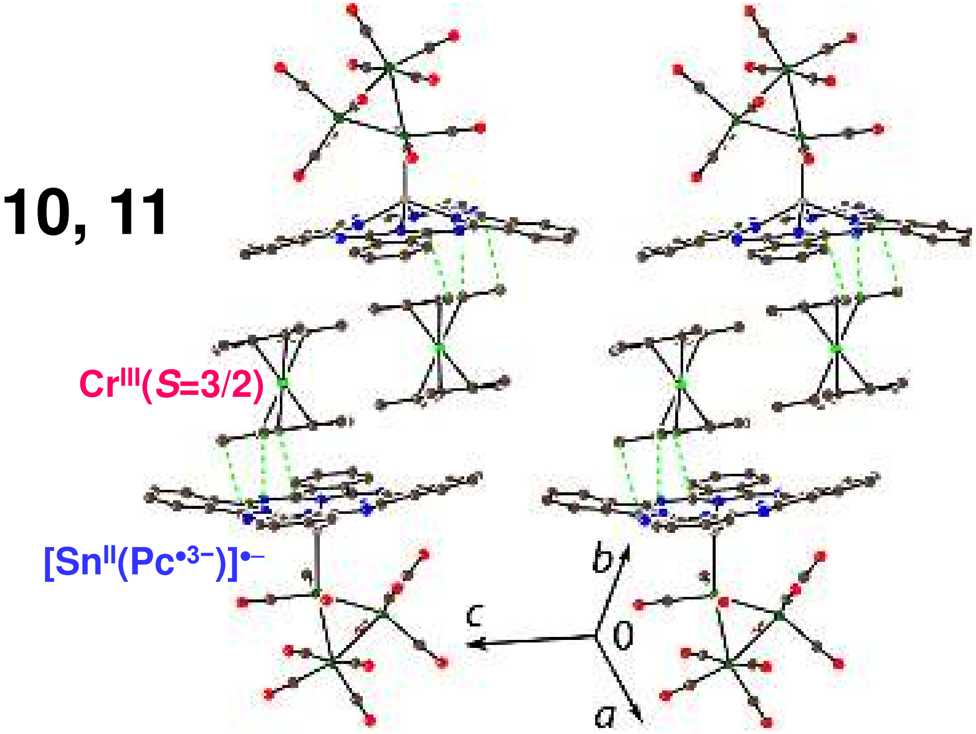
- The Heisenberg model for pairs of isolated antiferromagnetically coupled spins
- Qurie impurity (about 3 %)

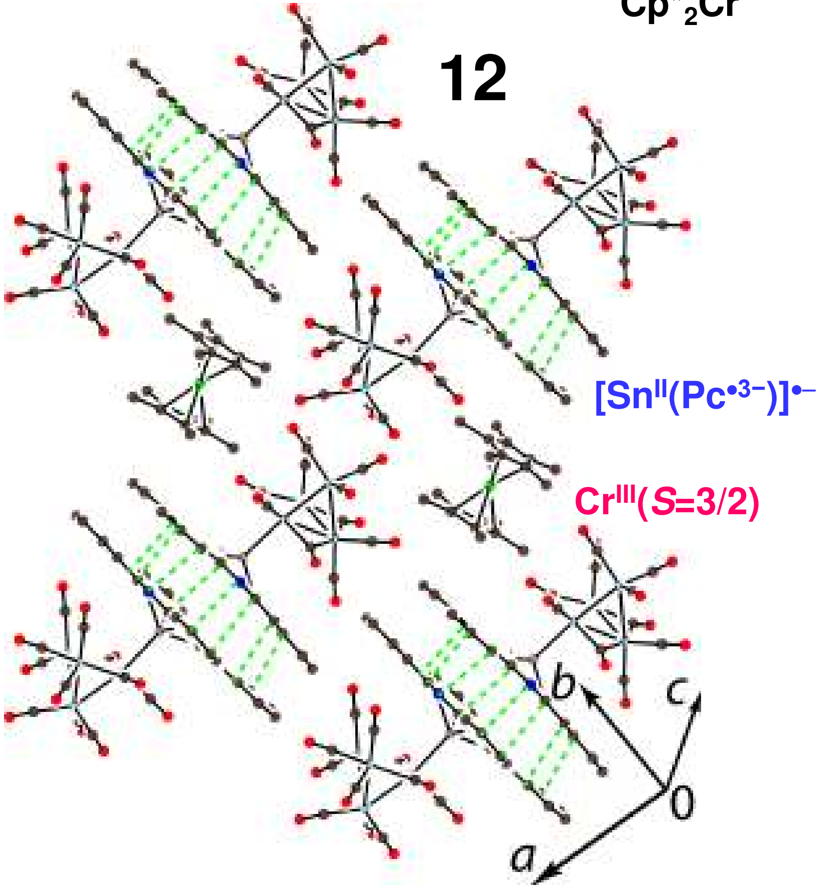
Multinuclear complexes

10	$(Cp^*_2Cr^+)\{\mathbf{Ru_3}(CO)_{11}\cdot\mathbf{Sn^{II}(Pc^{\bullet 3-})}\}^-$	$\mathbf{Cr^{III}}(S=3/2) + \mathbf{Pc^{\bullet 3-}}\ (S=1/2)$
11	$(Cp^*_2Cr^+)\{\mathbf{Os_3}(CO)_{10}Cl\cdot\mathbf{Sn^{II}(Pc^{\bullet 3-})}\}^-$	$\mathbf{Cr^{III}}(S=3/2) + \mathbf{Pc^{\bullet 3-}}\ (S=1/2)+\mathbf{Os^{I}}(S=1/2)$
12	$(Cp^*_2Cr^+)\{\mathbf{Ir_4}(CO)_{11}\cdot\mathbf{Sn^{II}(Pc^{\bullet 3-})}\}_2^-$	$\mathbf{Cr^{III}}(S=3/2) + \mathbf{Pc^{\bullet 3-}}\ (S=1/2)$



Cp^*_2Cr





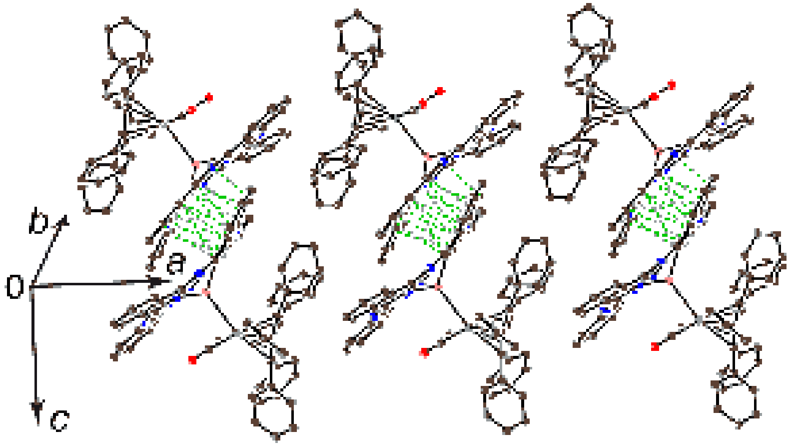
10: Θ = - 1.0 K

11: Θ = - 5.2, $Os^{I}(S=1/2)$

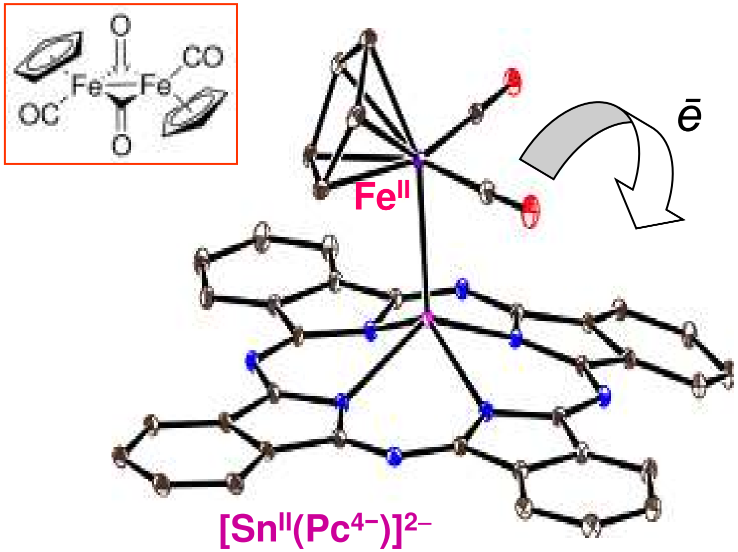
Perspective fields of research

Formally neutral closely packed complexes containing paramagnetic radical anions

Charge transfer from Fe^{I} to Pc^{2-} macrocycle with the formation of Fe^{II} and Pc^{4-} macrocycle



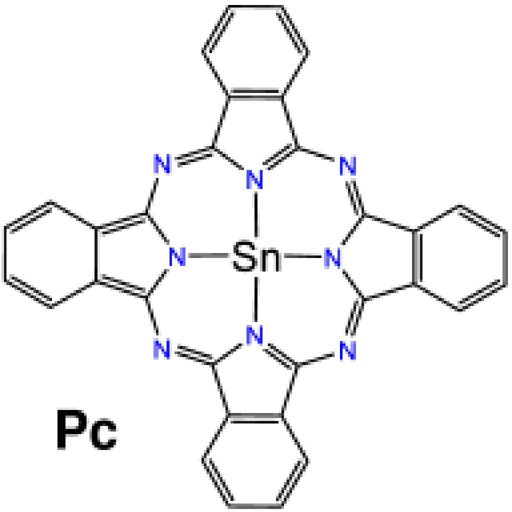
$\mathrm{Ph_5Cp\mathbf{Ru}^{II}(CO)_2\mathbf{[Sn^{II}(Pc^{\bullet 3-})]}}$ (**7**)



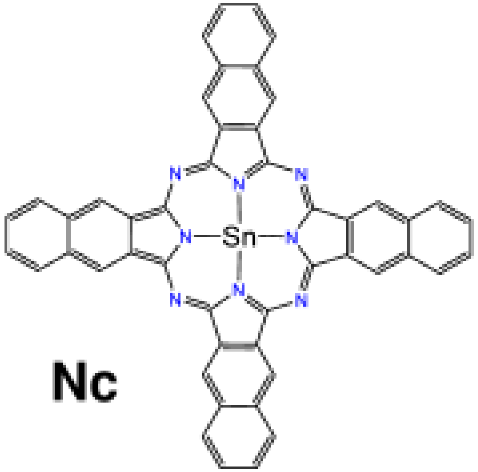
$\mathrm{\{cryptand(Na^+)\}\{Cp\mathbf{Fe}(CO)_2\mathbf{[Sn^{II}P^{4-}]}\}^-}$ (**3**)

Formally neutral complexes

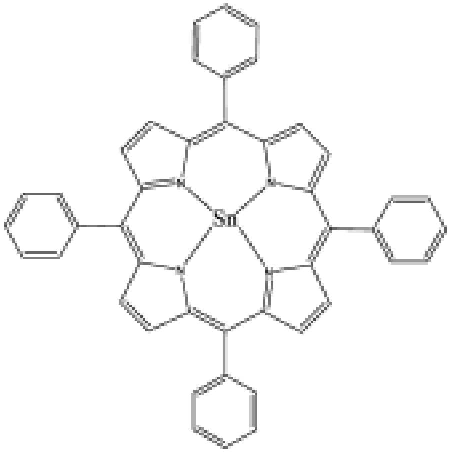
$Sn^{II}(Macrocycle^{2-})$ или $Sn^{IV}Cl_2(Macrocycle^{2-})$



Pc



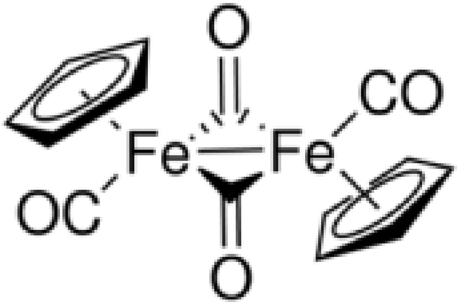
Nc



TPP

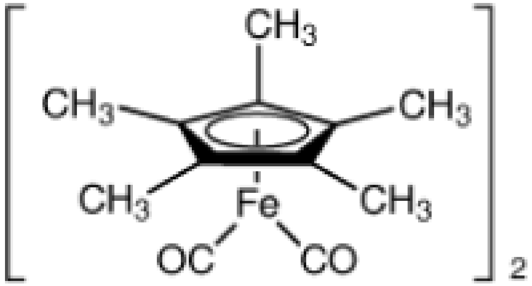
Acceptor properties of the macrocycles: Pc > Nc > TPP

Dalton Trans., 44, 13220 (2015)



$[CpFe^{I}(CO)_2]_2$

13	$\{CpFe^{II}(CO)_2[Sn^{II}(Pc^{\bullet 3-})]\}$
14	$\{Cp^{*}Fe^{II}(CO)_2[Sn^{II}(Pc^{\bullet 3-})]\}$
15	$\{Cp^{*}Fe^{II}(CO)_2[Sn^{II}(Nc^{\bullet 3-})]\}$
16	$\{CpFe^{II}(CO)_2[Sn^{II}(TPP^{\bullet 3-})]\}$

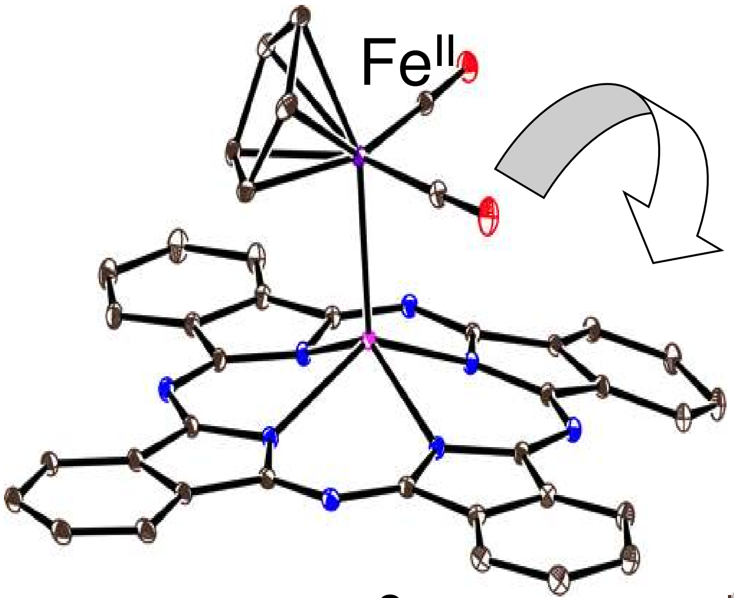


$[Cp^{*}Fe^{I}(CO)_2]_2$

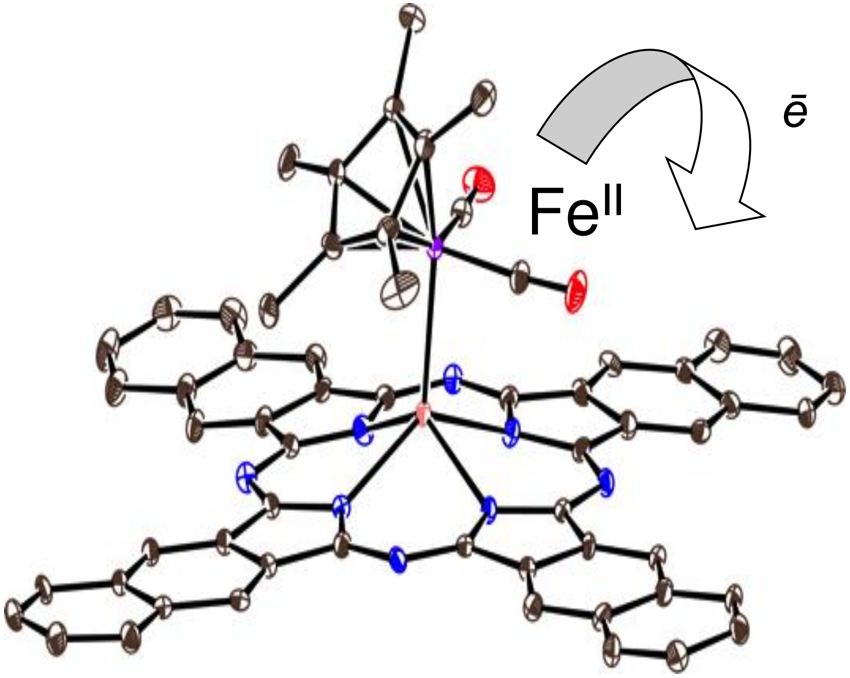
Intramolecular charge transfer

Charge ransfer from Fe^{I} to Macrocycle^{2-}

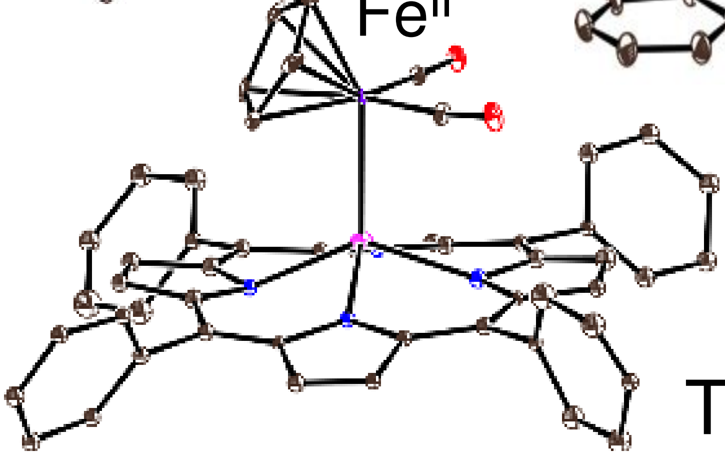
with the formation of diamagnetic Fe^{II} and paramagnetic Macrocycle$^{\bullet 3-}$



Pc$^{\bullet 3-}$

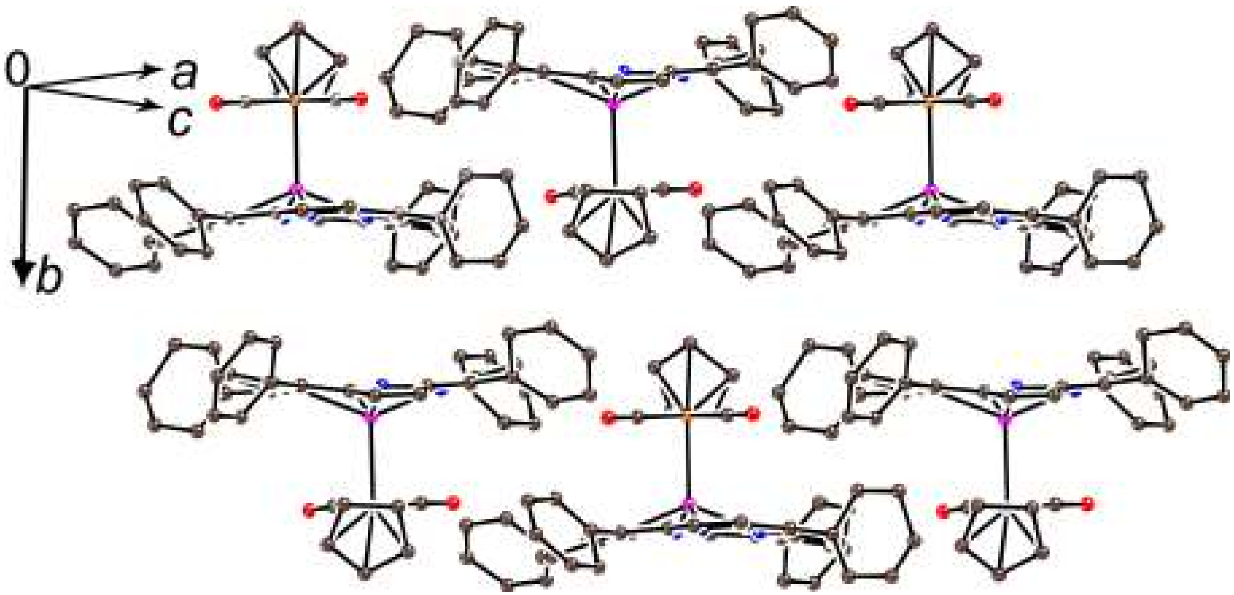


Nc$^{\bullet 3-}$



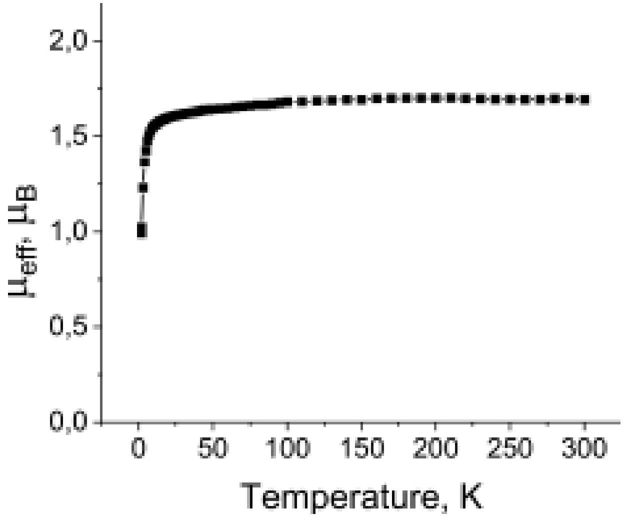
TPP$^{\bullet 3-}$

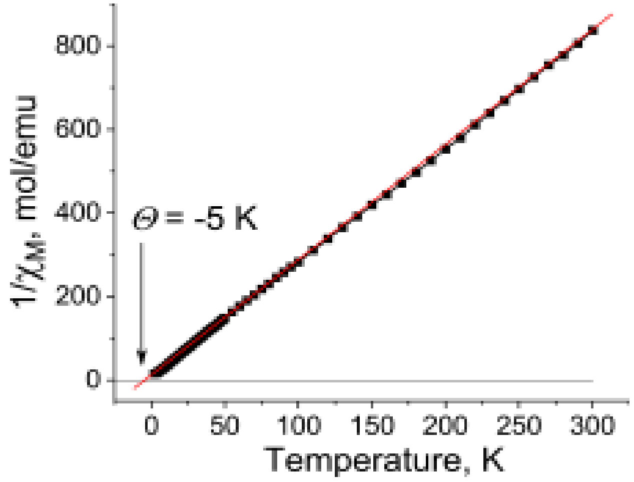
Porphyrin complex



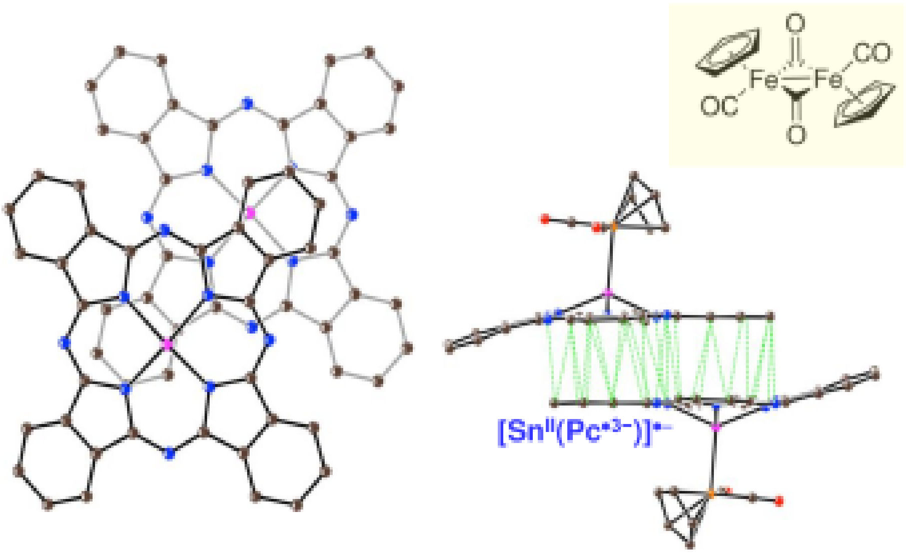
$\mathrm{CpFe^{II}(CO)_2\,Sn^{II}(}\mathbf{TPP}^{\bullet 3-}\mathrm{)}$ (**16**)

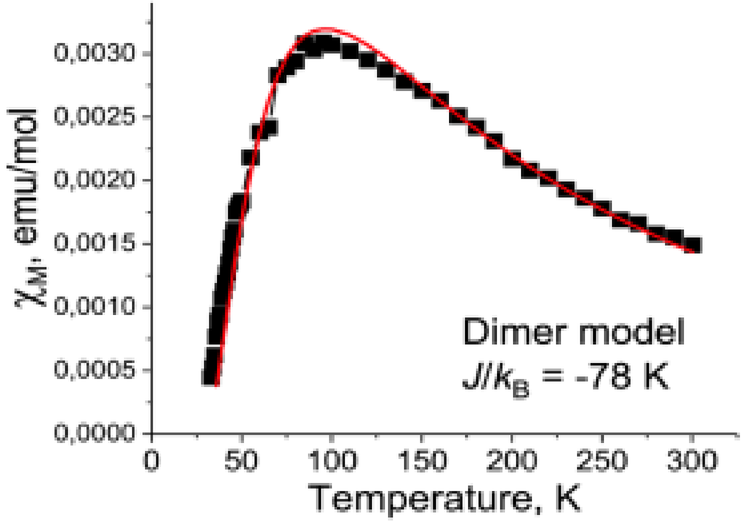
Rare example of crystalline complex based on reduced porphyrin $\mathbf{TPP}^{\bullet 3-}$



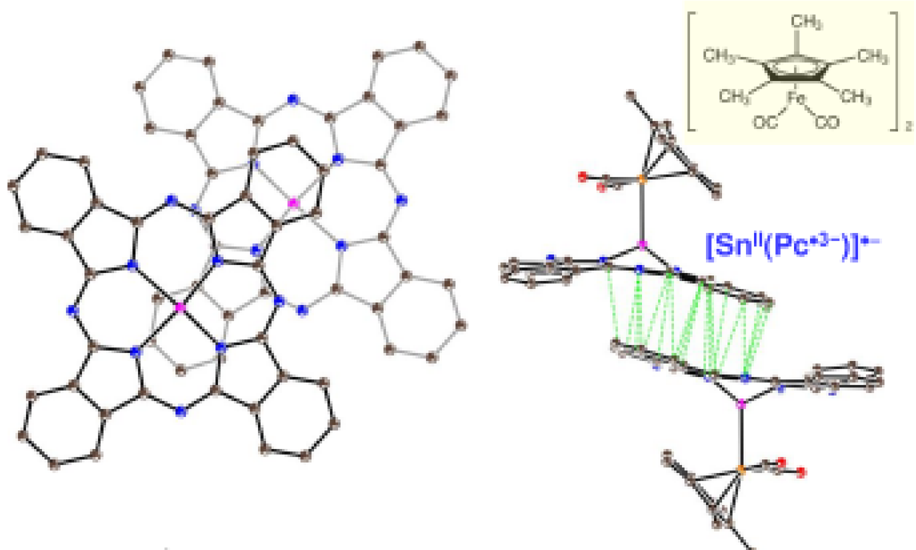


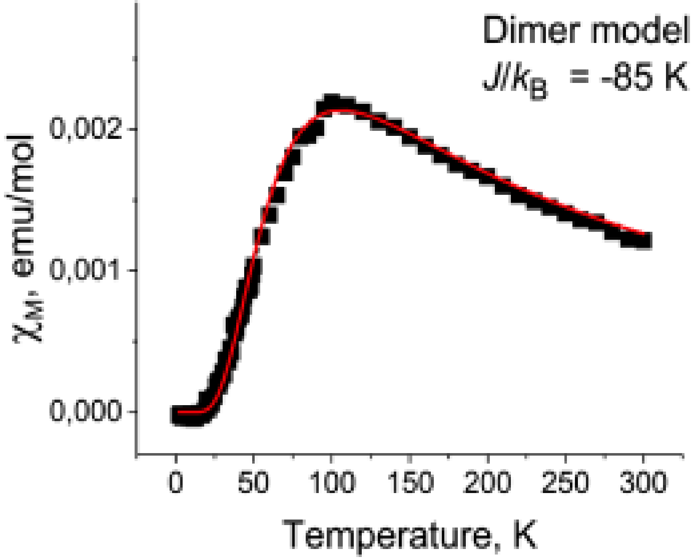
Pthalocyanine complexes





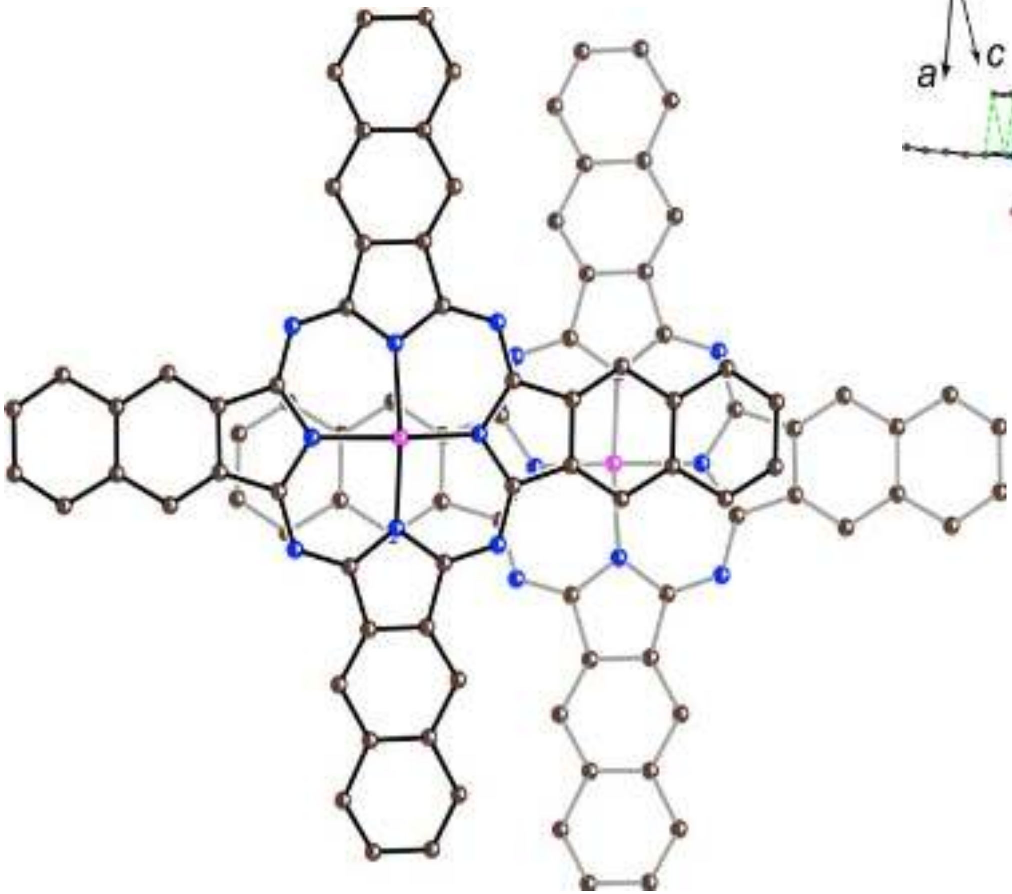
{$CpFe^{II}(CO)_2[Sn^{II}(\mathbf{Pc}^{\bullet 3-})]$} (**13**)

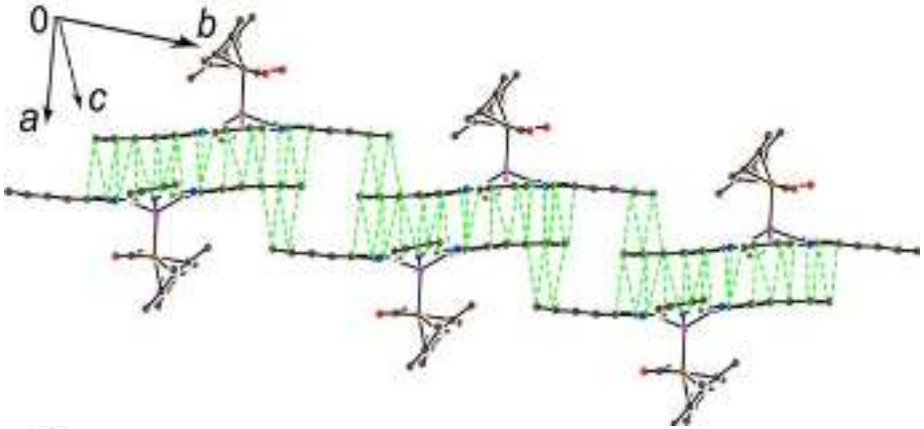


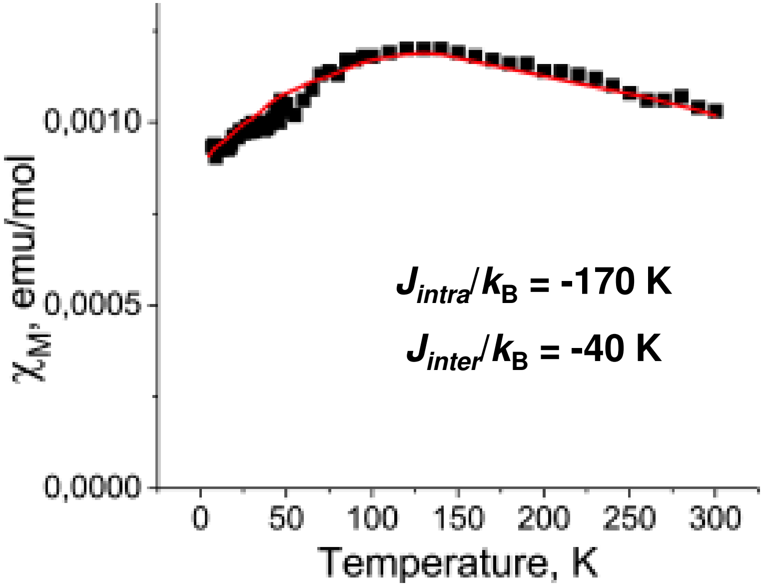


{$Cp^{*}Fe^{II}(CO)_2[Sn^{II}(\mathbf{Pc}^{\bullet 3-})]$} (**14**)

Naphhalocyanine complex







1D coupling in chains

$\{Cp^*Fe^{II}(CO)_2[Sn^{II}(\mathbf{Nc}^{\bullet 3-})]\}$ (**14**)

Conclusions

1. Methods for the preparation of σ-bonded coordination complexes of metal phthalocyanines have been developed;

2. A large series of crystalline complexes of tin(II) phthalocyanine in different charge states with transition metals and clusters has been obtained for the first time;

3. It has been shown that the reduced phthalocyanine macrocycle can act as a paramagnetic ligand for transition metals;

4. A series of formally neutral paramagnetic complexes has been obtained. Magnetic interactions are realized in dimers or chains in such complexes. It has been shown that the optical and magnetic properties of such systems can be "tuned" by using different macrocycles, as well as compounds of various transition metals.